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Effects of Tg and CTE on Semiconductor Encapsulants

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Abstract

As the role of direct-chip-attachment increases in the electronics industry, the reliability and performance of COB packaging materials becomes an increasing concern. Although many factors influence component reliability, the biggest determinants of performance are often the glass transition temperature (Tg) and the coefficient of thermal expansion (CTE) of the encapsulant or underfill. This paper discusses exactly what these properties are, how they are measured, and why they are important to device-reliability. Both materials and processes can impact these thermal properties. The nature of acrylate UV-cured materials versus thermally cured epoxies is examined and the significance of different cure parameters is discussed.

Introduction

The glass transition temperature and coefficient of thermal expansion of chip encapsulants have direct effects on semiconductor package performance and reliability.[1] Though they both are usually quoted and accepted as single numerical values, different methods of measurement and sample preparation will provide varying data for the same material. Even within the same sample, the glass transition occurs within a range of temperatures and not as a single point. Factors such as intrachain stiffness, polar forces, and comonomer compatability can affect the size of the glass transition region.[2] Thermal expansion coefficients are affected by polymer chain stiffness, packing, cure shrinkage and filler interactions.[3]

The purpose of this paper is to provide a summary of the common practices and techniques involved with Tg and CTE. Methods of measurement are explained and compared. Differences in sample preparation are shown to significantly affect results and suggest concerns about the performance of microelectronic packages. A better understanding of the factors affecting these material properties will allow process and design engineers to gain optimum performance from packaging encapsulants and become cognizent of the potential reliability changes that can occur from changes in board-level processing.

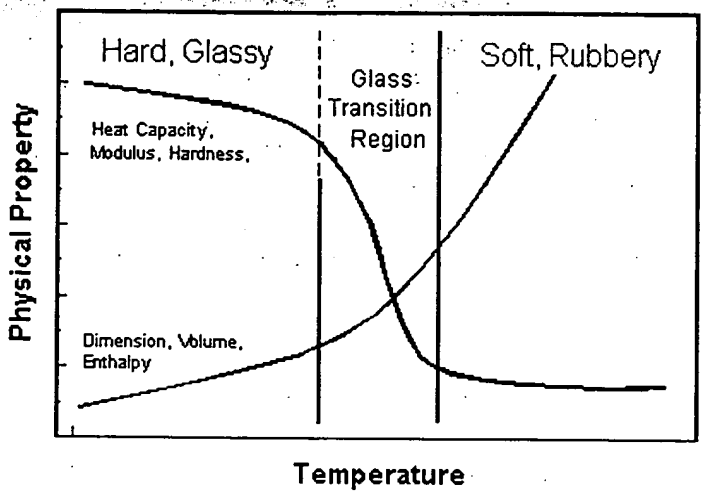
Instrumental Measurement

The glass transition temperature ("Tg") is the point where a substance changes from a hard-glassy material, to a soft-rubbery one. In monomer or thermoplastic polymers, the transition is from a solid or glass to a flowable liquid. For crosslinked thermosetting polymers, the transition is to a soft-rubbery composition and tends to occur across a thermal band rather than at a distinct point of temperature.

At the glass transition temperature, several easily measurable properties such as volume, dimension, enthalpy, strength and modulus also undergo transitions, and are often used to determine Tg's. Figure 1 schematically portrays the shifts in the glass transition region.

FIGURE 1

PROPERTY CHANGE



The property shifts at the glass transition temperature of encapsulants can cause severe stress buildup in packaged components leading to premature device failures[1]. Because of this, the Tg of the encapsulant usually places a limit on the use temperature and therefore becomes an important consideration when specifying for a particular application. Chemical composition and extent of cure are the major influences on Tg, however, the method of measurement can vary widely and will affect the data. The most commonly used analytical methods are compared in the following table.

Analytical Method Comparison

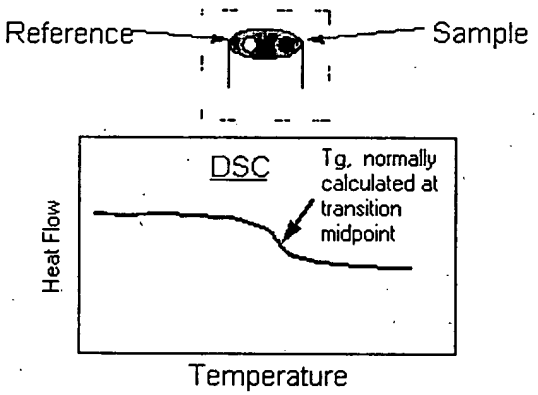
	Typical Run Time	Sample prep	Repeatability	Dependability	Comments
DSC	20 minutes	easy	good	marginal	Many materials do not exhibit clear transitions.
TMA	40 minutes	medium	fair	good	Very dependant on sample preparation.
DMA	120 minutes	difficult	excellent	excellent	Tg can be defined several different ways.

The coefficient of thermal expansion is a measure of the fractional change in dimension (usually thickness) per degree rise in temperature. For microelectronics encapsulants, it is often quoted in "ppm/°C" (value x 10-6/°C). Chemical composition, filler loading and cure cycles all affect the value. For typical materials that have non-linear expansion, the

specified temperature range will also have an effect on the data, with measurements out closer to the Tg yielding higher values than those quoted across lower temperature bands.

Differential scanning calorimetry (DSC) is the quickest and simplest test for Tg. The method requires extremely small samples (typically 5-20 mg) that require no special preparation, and material from components on processed boards can be utilized. The method consists of heating the sample in a closely calibrated thermocel where the temperature of the sample is compared to the temperature of a blank reference point within the same cell. Thermodynamic transitions such as melting points and reaction exotherms are easily measured, and the change in heat capacity at the Tg is seen as a shift in the baseline for cured encapsulants as shown in Figure 2.

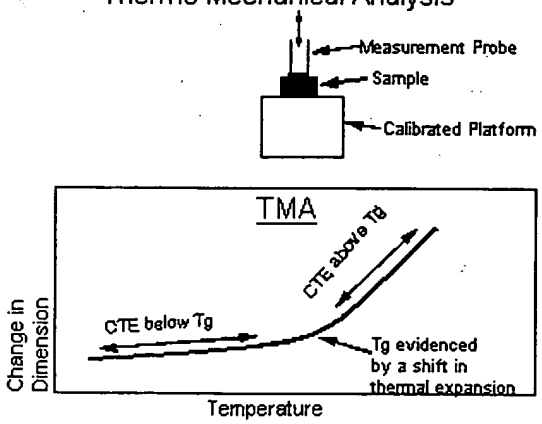
FIGURE 2
Differential Scanning Calorimetry



Unfortunately, this fast and convenient method is not universally applicable to all materials. High filler loadings, high crosslink densities, and other thermo-molecular processes can mask the shift due to the Tg and make the transition difficult or impossible to identify.

Thermo mechanical analysis (TMA) is the test used to determine thermal expansion coefficients. Since there is a shift to a higher thermal expansion coefficient above the Tg due to changes in molecular free volume[4], the method can also be used to measure the glass transition temperature as shown in Figure 3.

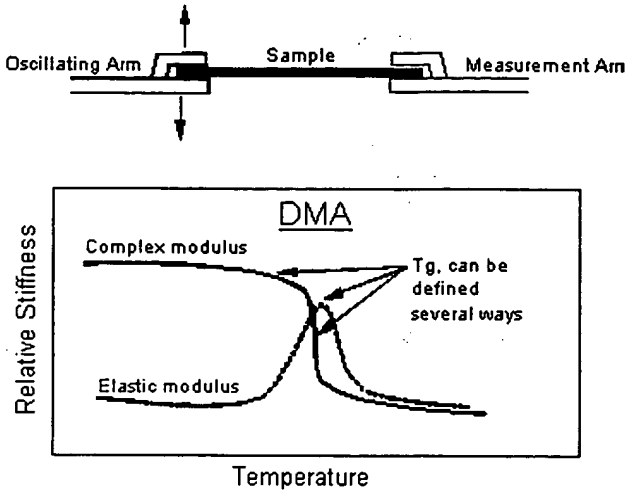
FIGURE 3
Thermo Mechanical Analysis



The technique simply consists of heating the sample upon an expansion-calibrated platform and measuring the dimensional change of the sample with an instrumented probe. The method will also easily follow cure-stress relaxations in and around the glass transition region which sometimes leads to ambiguity in assignment of a specific Tg and can yield a different value for the same specimen if measured at a different point (for instance, the cure stress may be significantly different when measured near the edge of a sample versus its center).

Dynamic mechanical analysis (DMA) consists of oscillating flexure energy applied to a rectangular bar of the cured encapsulant. The stress that is transferred through the specimen is measured as a function of temperature. Components of material stiffness are separated into a complex modulus and a rubbery modulus. The technique is highly accurate although the Tg can be defined in different ways which will have different values as illustrated in Figure 4.

FIGURE 4
Dynamic Mechanical Analysis



Large samples that must be accurately machined, coupled with longer setups make this test relatively expensive to run.

Each of the methods will produce different data for the same material as shown in the following table.

Instrument Effect on Glass Transition Temperature

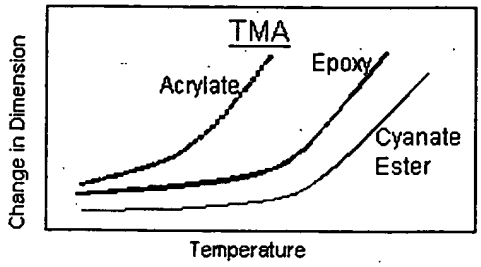
INSTRUMENT	GLASS TRANSITION TEMPERATURE
DSC	142°C
TMA	130°C
DMA	137°C (G") 146° (Tan delta)

A single specimen of a developmental epoxy encapsulant was cast and cured for 2 hours at 145°C after gelling at 100°C for one hour. It was then machined into specimens for DSC, TMA and DMA analysis. The results show Tg's ranging from 130°C for the TMA, to 146°C for the DMA measurement.

Discussion

The most obvious effect on the glass transition temperature and thermal expansion coefficient comes from the chemistry involved in the encapsulant. Figure 5 depicts a comparison of experimental epoxy, acrylate, and cyanate ester encapsulants.

FIGURE 5
Chemistry Effects

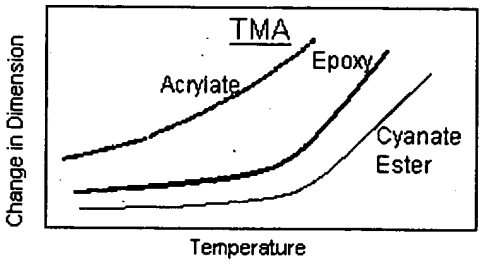


	ACRYLATE	EPOXY	CYANATE ESTER
Tg, °C	68	146	175
CTE, ppm/°C	66	24	18

All three were loaded with 75% of a proprietary low-expansion filler combination and thoroughly cured. The acrylate is a UV-curing system which incorporates a high flexibility/low modulus polymer backbone as evidenced by its low Tg. This sort of molecular architecture results in a relatively high CTE, even when the encapsulant is loaded with low-expansion filler. The epoxy is typical of current high reliability materials offering a reasonable Tg/CTE combination while the cyanate ester provides further improvements.

The following table shows the thermal expansions coefficients for the different materials encountered at the board level.

FIGURE 5
Chemistry Effects



	ACRYLATE	EPOXY	CYANATE ESTER
Tg, °C	<0°C	146	175
CTE, ppm/°C	86	24	18

Component stress from expansion mismatches is dispersed through the encapsulant when it closely matches the CTE of the board and associated metals. Stress is amplified and compounded when the encapsulant's CTE is high. Lowering the thermal expansion of chip on board encapsulants in order to more closely match expansions of the board, wafer, and solder junctions has been shown to have a direct effect in increasing package reliability. Since all useable encapsulant polymers have expansion coefficients several times larger than the materials to be protected, low expansion fillers are added. The filler loading level is normally as high as possible while retaining the necessary processability. The following table depicts the effect of different filler loading levels within the same material.

Effect of Filler Loading in an Epoxy Matrix

FILLER LOADING	TMA-Tg	CTE (25-100°C)
60 %	129°C	34.5 PPM/°C
65 %	127°C	28.8 PPM/°C
70 %	132°C	24.1 PPM/°C
75 %	130°C	20.0 PPM/°C
80 %	Unprocessable	--

The matrix consists of a standard epoxy anhydride which is loaded with a proprietary mixture of low expansion fillers. All samples were cured for 2 hours at 145°C after gelling for 1 hour at 100°C. CTE's decrease rapidly and the viscosity increases while the effect on Tg is negligible.

Cure temperature affects the extent of cure, the rate of gellation and the cure stress which is a function of the gellation temperature. As a result, the cure temperature influences both the coefficient of thermal expansion and the Tg of the encapsulant. As cure temperature increases, crosslink density and degree of cure increase. Since the glass transition is a function of both, the Tg undergoes a corresponding rise until a point where nearly all polymer reaction sites have been used. At that point, the glass transition temperature plateaus with further temperature increase unless thermo-degradation begins. The following table illustrates the point, where increasing the cure temperature from 130°C to 175°C increases the Tg of the encapsulant from 117°C up to 146°C. At the same time, the CTE increases from 22.9 ppm/°C to 24.3 ppm/°C.

Cure Temperature Effects

CURE TEMP	TMA-Tg	CTE (25-100°C)
130°C / 2 HOURS	117°C	22.9 ppm/°C
146°C / 2 HOURS	127°C	23.8 ppm/°C
160°C / 2 HOURS	137°C	26.3 ppm/°C
175°C / 2 HOURS	146°C	24.3 ppm/°C
PREGEL + 130°C	113°C	21.1 ppm/°C
PREGEL + 145°C	130°C	20.0 ppm/°C
PREGEL + 160°C	138°C	19.6 ppm/°C
PREGEL + 175°C	140°C	19.4 ppm/°C

The increase in coefficient of thermal expansion is due to higher levels of cure stress being built into the samples as the temperature increases. The cure stress is a function of gellation temperature because the faster that the material gels, the more likely it is for polymer chains to become locked into stressed configurations and the more that shrinkage will occur as the sample cools after cure. Since it is ultimately desirable to have both a high Tg and a low CTE, encapsulants are often gelled at temperatures significantly lower than the cure temperature. Once the encapsulant has gelled, more time at higher temperatures actually decreases stress through an annealing process and results in significantly lower CTE's.

The amount of time at temperature also has an effect. The following table shows the results of cure time experiments carried out on a developmental anhydride-cured epoxy encapsulant.

Cure Temperature Effects

CURE TEMP	TMA Tg	CTE (25-100°C)
130°C / 2 HOURS	117°C	22.9 ppm/°C
145°C / 2 HOURS	127°C	23.8 ppm/°C
160°C / 2 HOURS	137°C	26.3 ppm/°C
175°C / 2 HOURS	146°C	24.3 ppm/°C
PREGEL + 130°C	113°C	21.1 ppm/°C
PREGEL + 145°C	130°C	20.0 ppm/°C
PREGEL + 160°C	138°C	19.6 ppm/°C
PREGEL + 175°C	140°C	19.4 ppm/°C

Between 0.5 and 2.0 hours at 160°C, Tg and CTE both increase with the increasing extent of cure. Considerable cure stress is built up in the process as discussed earlier. Once the material is fully cured, additional time at temperature allows a slow relaxation of chains trapped in stressed configurations resulting in significant lowering of the CTE without further increase in Tg. Although this type of cure is unrealistic from a processing standpoint, it does illustrate the type of performance that can be ultimately achieved.

Summary

The glass transition temperature and coefficient of thermal expansion for COB encapsulants have been shown to not exist as single numbers, but as ranges of values that are very dependent on measurement techniques and processing methodology. Designing from data developed under different conditions than those seen at the board level will very likely be in error and caution is urged. Cure parameters have a significant impact on the data, and should be noted for any reference to a material's CTE or Tg. Property comparisons must be made on materials that have been processed and tested in similar manners to be meaningful.

References

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